



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US90/07669 <b>(22) International Filing Date:</b> 27 December 1990 (27.12.90)  <b>(30) Priority data:</b> 459,921 2 January 1990 (02.01.90) US  <b>(71) Applicant:</b> EXXON CHEMICAL PATENTS INC. [US/ US]; 1900 East Linden Avenue, Linden, NJ 07036-0710 (US).  <b>(72) Inventors:</b> HLATKY, Gregory, George ; 1114 Indian Au- turnn, Houston, TX 77062 (US). UPTON, David, Jona- than ; 706 Glenmore, Pasadena, TX 77503 (US). TURN- ER, Howard, William ; 303 Elder Glen, Webster, TX 77598 (US).		<b>(74) Agents:</b> KURTZMAN, Myron, B. et al.; Exxon Chemical Company, 5200 Bayway Drive, Baytown, TX 77522-5200 (US).  <b>(81) Designated States:</b> AT (European patent), AU, BE (Euro- pean patent), BR, CA, CH (European patent), DE (Eu- ropean patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European pa- tent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), SU.  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> SUPPORTED IONIC METALLOCENE CATALYSTS FOR OLEFIN POLYMERIZATION  <b>(57) Abstract</b>  A supported catalyst for olefin polymerization comprising a Group IV-B metallocene component and an ionic activator component comprising a cation capable of donating a proton and a labile bulky anion having a plurality of lipophilic radicals so that the anion is sterically hindered from covalently bonding with a cation produced from the Group IV-B metal of the metallocene.		

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SUPPORTED IONIC METALLOCENE CATALYSTS  
FOR OLEFIN POLYMERIZATION

Background of the Invention

1. Field of the Invention

1           The invention relates to supported catalysts for  
2 polymerization of olefins including gas or slurry phase  
3 polymerization of olefins, diolefins, cyclic olefins and  
4 acetylenically unsaturated monomers. These catalysts, which may be  
5 supported on known catalyst supports, include a Group IV-B metal  
6 metallocene compound and an ionic activator compound. While the  
7 homogeneous variant of this catalyst system has been previously  
8 disclosed in copending U.S. Serial No. 133,480, a supported form of  
9 the catalyst system has not heretofore been produced. The supported  
10 catalyst, suitable for use in gas or slurry phase olefin  
11 polymerization, provides a polymer product having a narrower particle  
12 size distribution and higher bulk density than achievable with the  
13 homogeneous catalyst system. Furthermore, the use of the supported

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1 catalyst in the gas phase results in greatly reduced reactor fouling  
2 as compared to the unsupported or homogeneous variant. By employing  
3 suitably sized supports, the catalyst system can be employed in  
4 solution and high pressure polymerization processes.  
5

## 2. Background

6 Ziegler-Natta type catalysts for the polymerization of  
7 olefins are well known. The traditional Ziegler-Natta type systems  
8 comprise a metal halide activated to a catalyst species by reaction  
9 with a metal alkyl cocatalyst, particularly an aluminum alkyl  
10 cocatalyst. The activation of these traditional Ziegler-Natta  
11 catalysts generates a variety of different active sites. As a  
12 consequence of this non-uniformity of the active sites, the catalysts  
13 produce polymer products of broad molecular weight distribution  
14 (MWD). Furthermore, the copolymer products exhibit broad composition  
15 distribution (CD), poor comonomer incorporation and blocky sequence  
16 distribution.

17 Recently it has been found that active catalysts are formed  
18 when a bis(cyclopentadienyl) compound of the Group IV-B metals, in  
19 particular zirconium and hafnium, is activated by an alumoxane. The  
20 metallocene-alumoxane catalysts whether homogeneous or supported  
21 generally possess high activity and are more versatile than  
22 conventional Ziegler-Natta catalysts in that they may be effectively  
23 used to produce a variety of polymer products including, for example,  
24 high density linear polyethylene (HDPE), linear low density  
25 polyethylene (LLDPE), ethylene-propylene copolymer (EP),  
26 non-crystalline polypropylene and crystalline polypropylene. The  
27 metallocene-alumoxane catalysts also offer the significant advantage  
28 over the traditional Ziegler-Natta catalysts of being able to produce  
29 polymers with narrow MWD.

30 While the metallocene-alumoxane catalysts do offer  
31 significant advantages over the traditional Ziegler-Natta catalysts,  
32 they nevertheless have limitations in practical commercial  
33 applications. These limitations include the relatively high cost of  
34 the alumoxane cocatalysts. Alumoxane is also air sensitive and

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1 difficult to manipulate. Furthermore, the metallocene-alumoxane  
2 catalysts, while producing a narrow MWD polymer product, have a  
3 limited capability to produce high molecular weight polymers or  
4 polymers having a high comonomer content.

5 Copending U.S. Patent Application Serial No. 133,480, also  
6 published as European Patent Application 277,004 which is hereby  
7 incorporated by reference, describes a further advance in metallocene  
8 catalysts: a new metallocene catalyst which does not require either  
9 an alkyl aluminum or an alumoxane as an activator. The Group IV-B  
10 metallocene catalyst is prepared as a reaction product of a Group  
11 IV-B metal metallocene compound and an ionic activator compound. The  
12 ionic activator comprises a cation having a donatable proton and a  
13 labile, bulky anion which is a single coordination complex having a  
14 plurality of lipophilic radicals covalently coordinated to and  
15 shielding a central charge-bearing metal or metalloid atom, the bulk  
16 of said anion being such that upon reaction of the activator cation  
17 donatable proton with a proton reactable substituent of a  
18 bis(cyclopentadienyl) Group IV-B metal compound to form a Group IV-B  
19 metal cation, the anion of the activator is sterically hindered from  
20 covalently coordinating to the Group IV-B metal cation. Hence, as  
21 described in the copending application, an active catalytic species  
22 of a metallocene is formed, namely an ionic pair comprising a  
23 metallocene transition metal cation paired with a noncoordinating  
24 anion of the activator component.

25 The new metallocene catalyst system (hereafter referred to  
26 as an "ionic metallocene catalyst") eliminates the need for an  
27 expensive alumoxane activator. The ionic metallocene catalyst also  
28 offers other advantages over the metallocene-alumoxane catalysts such  
29 as permitting the production of polyolefin products of narrow MWD and  
30 of significantly higher weight average molecular weight at high rates  
31 of catalytic activity while also permitting better incorporation of  
32 comonomers and the control of the chain end chemistry of the polymer

33 The new ionic metallocene catalyst of the copending  
34 application is, however, a homogeneous catalyst and generally can not  
35 be practically used for gas phase polymerization. The use of a

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1 supported catalyst offers the possibility of gas phase  
2 compatibility. Control of the particle size distribution of the  
3 polymeric product in the various polymerization processes eliminates  
4 or reduces the extent of reactor fouling.

5 Supported catalysts for olefin polymerization are well known  
6 in the art. These catalysts offer, among others, the advantages of  
7 being usable in gas or slurry phase reactors allowing the control of  
8 polymer particle size and thereby the control of product bulk  
9 density. Gas phase reactors also eliminate the need for a solvent  
10 and the equipment for solvent handling and separation. However, the  
11 known Ziegler-Natta olefin polymerization supported catalysts also  
12 present disadvantages which include broad MWD and composition  
13 distribution (CD), inefficient incorporation of comonomers, poor  
14 sequence distribution and, in the case of lower activity catalysts,  
15 the need for a product deashing step.

16 Supported metallocene-alumoxane catalysts for olefin  
17 polymerization are described in U.S. Patent 4,701,432 of Welborn.  
18 These supported metallocene-alumoxane catalysts are obtained by  
19 reacting a metallocene and an alumoxane in the presence of the solid  
20 support material. The supported catalyst may then be employed either  
21 as the sole catalyst component or may be employed in combination with  
22 an organometallic cocatalyst. The supported metallocene-alumoxane  
23 catalyst, however, still produces polymers of generally lower  
24 molecular weight and comonomer incorporation than desired for certain  
25 applications.

26 It would be desirable to provide a supported catalyst for  
27 gas or slurry phase olefin polymerization that eliminates the need  
28 for either an alumoxane or an alkyl aluminum cocatalyst. It would be  
29 further desirable that such supported catalyst be capable of  
30 providing a polymer product having a high molecular weight, narrow  
31 MWD and CD, good comonomer incorporation, good sequence distribution,  
32 high bulk density and controlled particle size for ease of removal  
33 from the reactor.

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Summary

1           The invention provides a supported ionic metallocene  
2 catalyst which is suitable for use in the polymerization of olefins  
3 including gas or slurry phase polymerization of olefins. The  
4 heterogeneous catalyst, like its homogeneous counterpart disclosed in  
5 our European Patent Application EP 277 004, permits the production of  
6 polyolefins of high molecular weight and narrow molecular weight  
7 distribution (MWD) at high rates. Moreover, the polyolefin products  
8 of the supported catalyst have a narrow composition distribution (CD)  
9 and improved sequence distribution of comonomers as compared to the  
10 products of prior art conventional supported Ziegler-Natta catalysts.

11           The possibility of producing a supported catalyst was  
12 surprising since it would have been predicted that the reaction of  
13 ionic catalyst as described in the copending application with a Lewis  
14 base such as is present on a metal oxide surface would result in  
15 catalyst deactivation. This invention is even more surprising since  
16 aluminum alkyls are not present during catalyst preparation and  
17 furthermore the polymer products are similar to that obtained with  
18 the unsupported catalyst.

19           The supported ionic metallocene catalyst of this invention  
20 comprises the ionic metallocene catalyst and a suitable support  
21 material. The metallocene component of the ionic metallocene  
22 catalyst may be selected from a bis(cyclopentadienyl) derivative of a  
23 Group IV-B (Periodic Table of Elements, published and copyrighted by  
24 CRC Press, Inc., 1984) metal compound containing at least one ligand  
25 which will combine with an activator component or at least a portion  
26 thereof such as a cation portion thereof. The activator component is  
27 an ionic compound comprising a cation which will irreversibly react  
28 with at least one ligand contained in said Group IV-B metal compound  
29 (metallocene component) and an anion which is a single coordination  
30 complex comprising a plurality of lipophilic radicals covalently  
31 coordinated to and shielding a central formally charge-bearing metal  
32 or metalloid atom, which anion is bulky, labile and stable to any  
33 reaction involving the cation of the activator component. The  
34 charge-bearing metal or metalloid may be any metal or metalloid

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1 capable of forming a coordination complex which is not hydrolyzed by  
2 aqueous solutions. Upon combination of the metallocene component and  
3 activator component, the cation of the activator component reacts  
4 with one of the ligands of the metallocene component, thereby  
5 generating an ion pair consisting of a Group IV-B metal cation with a  
6 formal coordination number of 3 and a valence of +4 and the  
7 aforementioned anion, which anion is compatible with and  
8 noncoordinating toward the metal cation formed from the metallocene  
9 component. The anion of the activator compound must be capable of  
10 stabilizing the Group IV-B metal cation complex without interfering  
11 with the ability of the Group IV-B metal cation or its decomposition  
12 product to function as a catalyst and must be sufficiently labile to  
13 permit displacement by an olefin, diolefin or an acetylenically  
14 unsaturated monomer during polymerization.

15         Either the ionic metallocene catalyst or both its components  
16 will be contacted with an inorganic or organic solid support  
17 material, either thermally or chemically dehydrated before such  
18 contact, to form the supported ionic metallocene catalyst of this  
19 invention.

20         The method for preparing these supported ionic catalyst  
21 comprises the steps of,

22         (a) combining, in a solvent or diluent

23                 (i) at least one metallocene component comprising a  
24 bis(cyclopentadienyl) metal compound containing at least one ligand  
25 capable of reacting with a proton, said metal being selected from  
26 Group IV B metals,

27                 (ii) at least one activator component comprising a  
28 cation capable of donating a proton and an anion, said anion being a  
29 single coordination complex comprising a plurality of lipophilic  
30 radicals covalently coordinated to and shielding a central  
31 charge-bearing metal or metalloid atom, said anion being bulky,  
32 labile and capable of stabilizing the metal cation formed as a result  
33 of reaction between the two, and

34                 (iii) a catalyst support material suspended in a  
35 suitable solvent, and

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1 (b) recovering a supported catalyst product as a  
2 free-flowing solid or slurry.

3 The supported catalyst of this invention will polymerize  
4 olefins, diolefins and/or acetylenically unsaturated monomers either  
5 alone or in combination with other olefins and/or other unsaturated  
6 monomers in liquid, slurry or gas phase reactions.

7 In general, catalysts can be selected so as to produce the  
8 polymer products which will be free of certain trace elements  
9 generally found in polymers produced with Ziegler-Natta type  
10 catalysts such as aluminum, magnesium, chloride and the like. The  
11 polymer products produced with the catalysts of this invention  
12 should, then, have a broader range of applications than polymers  
13 produced with either the more conventional Ziegler-Natta type  
14 catalysts containing a metal alkyl, such as an aluminum alkyl, or the  
15 metallocene-alumoxane catalysts.

#### 16 Detailed Description of the Preferred Embodiments

17 The present invention relates to supported catalysts  
18 eminently suited for use in various polymerization processes  
19 including gas or slurry phase polymerization of olefins. The  
20 heterogeneous catalyst includes a metallocene of the Group IV-B  
21 transition metals, an ionic activator compound and a catalyst  
22 support. European Patent Application EP 277,004 incorporated by  
23 reference, describes the homogeneous variant of the Group IV-B ionic  
24 metallocene catalyst which is prepared as the reaction product of a  
25 Group IV-B metal metallocene compound and an ionic activator compound.

#### The Metallocene Component

26 The Group IV-B metal compounds, particularly the titanium,  
27 zirconium and hafnium compounds, useful as first compounds in the  
28 ionic metallocene catalyst system employed in the process of this  
29 invention are the bis(cyclopentadienyl) derivatives of titanium,  
30 zirconium or hafnium. In general, such useful titanium, zirconium  
31 and hafnium compounds may be represented by the following general  
32 formulae:

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- 1           1.  $(A-Cp)MX_1X_2$
- 2           2.  $(A-Cp)\overline{MX'_1X'_2}$
- 3           3.  $(A-Cp)ML$
- 4           4.  $(Cp^*)(CpR)\overline{MX_1}$

5 wherein: M is a metal selected from the Group consisting of titanium  
 6 (Ti), zirconium (Zr) and hafnium (Hf); (A-Cp) is either (Cp)(Cp\*) or  
 7 Cp-A'-Cp\* and Cp and Cp\* are the same or different substituted or  
 8 unsubstituted cyclopentadienyl radicals, and wherein A' is a covalent  
 9 bridging group containing a Group IV-A element; L is an olefin,  
 10 diolefin or aryne ligand;  $X_1$  and  $X_2$  are, independently,  
 11 selected from the group consisting of hydride radicals, hydrocarbyl  
 12 radicals having from 1 to about 20 carbon atoms,  
 13 substituted-hydrocarbyl radicals, wherein 1 or more of the hydrogen  
 14 atoms are replaced with a halogen atom, having from 1 to about 20  
 15 carbon atoms, organo-metalloid radicals comprising a Group IV-A  
 16 element wherein each of the hydrocarbyl substituents contained in the  
 17 organo-portion of said organo-metalloid, independently, contain from  
 18 1 to about 20 carbon atoms and the like;  $X'_1$  and  $X'_2$  are  
 19 joined and bound to the metal atom to form a metallacycle, in which  
 20 the metal,  $X'_1$  and  $X'_2$  form a hydrocarbocyclic ring  
 21 containing from about 3 to about 20 carbon atoms; and R is a  
 22 substituent, preferably a hydrocarbyl substituent, having from 1 to  
 23 20 carbon atoms, on one of the cyclopentadienyl radicals which is  
 24 also bound to the metal atom. Each carbon atom in the  
 25 cyclopentadienyl radical may be, independently, unsubstituted or  
 26 substituted with the same or a different radical selected from the  
 27 Group consisting of hydrocarbyl radicals, substituted-hydrocarbyl  
 28 radicals wherein one or more hydrogen atoms is replaced by a halogen  
 29 atom, hydrocarbyl-substituted metalloid radicals wherein the  
 30 metalloid is selected from Group IV-A of the Periodic Table of the  
 31 Elements, halogen radicals and the like. Suitable hydrocarbyl and

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1 substituted-hydrocarbyl radicals which may be substituted for at  
2 least one hydrogen atom in the cyclopentadienyl radical will contain  
3 from 1 to about 20 carbon atoms and include straight and branched  
4 alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic  
5 hydrocarbon radicals, aromatic radicals and alkyl-substituted  
6 aromatic radicals. Similarly, and when  $X_1$  and/or  $X_2$  is a  
7 hydrocarbyl or substituted-hydrocarbyl radical, each may,  
8 independently, contain from 1 to about 20 carbon atoms and be a  
9 straight or branched alkyl radical, a cyclic hydrocarbyl radical, an  
10 alkyl-substituted cyclic hydrocarbyl radical, an aromatic radical or  
11 an alkyl-substituted aromatic radical. Suitable organometalloid  
12 radicals include mono-, di- and trisubstituted organometalloid  
13 radicals of Group IV-A elements wherein each of the hydrocarbyl  
14 Groups contain from 1 to about 20 carbon atoms. Suitable  
15 organometalloid radicals include trimethylsilyl, triethylsilyl,  
16 ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl,  
17 trimethylgermyl and the like.

18         Illustrative, but not limiting examples of  
19 bis(cyclopentadienyl)zirconium compounds which may be used in the  
20 preparation of the improved  
21 (ethylcyclopentadienyl)(cyclopentadienyl) and  
22 bis(ethylcyclopentadienyl)zirconium dihydride,  
23 (propylcyclopentadienyl)(cyclopentadienyl) and  
24 bis(propylcyclopentadienyl)zirconium dihydride,  
25 (n-butylcyclopentadienyl)(cyclopentadienyl) and  
26 bis(n-butylcyclopentadienyl)zirconium dihydride,  
27 (t-butylcyclopentadienyl)(cyclopentadienyl) and  
28 bis(t-butylcyclopentadienyl)zirconium dihydride,  
29 (cyclohexylmethylcyclopentadienyl)(cyclopentadienyl) and  
30 bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,  
31 (benzylcyclopentadienyl)(cyclopentadienyl) and  
32 bis(benzylcyclopentadienyl)zirconium dihydride,  
33 (diphenylmethylcyclopentadienyl)(cyclopentadienyl) and  
34 bis(diphenylmethylcyclopentadienyl)zirconium dihydride and the like;  
35 (polyhydrocarbyl-substituted-cyclopentadienyl) zirconium compounds

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1 such as (dimethylcyclopentadienyl) (cyclopentadienyl) and  
2 bis(dimethylcyclopentadienyl) zirconium dimethyl,  
3 (trimethylcyclopentadienyl) (cyclopentadienyl) and  
4 bis(trimethylcyclopentadienyl) zirconium dimethyl,  
5 (tetramethylcyclopentadienyl) (cyclopentadienyl) and  
6 bis(tetramethylcyclopentadienyl) zirconium dimethyl,  
7 (permethylcyclopentadienyl) (cyclopentadienyl) and  
8 bis(permethylcyclopentadienyl) zirconium dimethyl,  
9 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and  
10 bis(ethyltetramethylcyclopentadienyl) zirconium dimethyl,  
11 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dimethyl,  
12 (dimethylcyclopentadienyl) (cyclopentadienyl) and  
13 bis(dimethylcyclopentadienyl) zirconium dihydride,  
14 (trimethylcyclopentadienyl) (cyclopentadienyl) and  
15 bis(trimethylcyclopentadienyl) zirconium dihydride,  
16 (tetramethylcyclopentadienyl) (cyclopentadienyl) and  
17 bis(tetramethylcyclopentadienyl)zirconium dihydride,  
18 (permethylcyclopentadienyl) (cyclopentadienyl) and  
19 bis(permethylcyclopentadienyl)zirconium dihydride,  
20 (ethyltetramethylcyclopentadienyl) (cyclopentadienyl) and  
21 bis(ethyltetramethylcyclopentadienyl)zirconium dihydride,  
22 (indenyl)(cyclopentadienyl) and bis(indenyl)zirconium dihydride  
23 (propylcyclopentadienyl) (cyclopentadienyl) and  
24 bis(propylcyclopentadienyl)zirconium dihydride,  
25 (n-butylcyclopentadienyl) (cyclopentadienyl) and  
26 bis(n-butylcyclopentadienyl)zirconium dihydride,  
27 (t-butylcyclopentadienyl) (cyclopentadienyl) and  
28 bis(t-butylcyclopentadienyl)zirconium dihydride,  
29 (cyclohexylmethylcyclopentadienyl) (cyclopentadienyl) and  
30 bis(cyclohexylmethylcyclopentadienyl)zirconium dihydride,  
31 (benzylcyclopentadienyl) (cyclopentadienyl) and  
32 bis(benzylcyclopentadienyl)zirconium dihydride,  
33 (diphenylmethylcyclopentadienyl) (cyclopentadienyl) and  
34 bis(diphenylmethylcyclopentadienyl)zirconium dihydride and the like;  
35 (metal hydrocarbyl-substituted cyclopentadienyl)zirconium compounds

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1 such as (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and  
2 bis(trimethylsilylcyclopentadienyl)zirconium dimethyl,  
3 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and  
4 bis(trimethylgermylcyclopentadienyl)zirconium dimethyl,  
5 (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and  
6 bis(trimethylstannylcyclopentadienyl)zirconium dimethyl,  
7 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and  
8 bis(trimethylplumbylcyclopentadienyl)zirconium dimethyl,  
9 (trimethylsilylcyclopentadienyl)(cyclopentadienyl) and  
10 bis(trimethylsilylcyclopentadienyl)zirconium dihydride,  
11 (trimethylgermylcyclopentadienyl)(cyclopentadienyl) and  
12 bis(trimethylgermylcyclopentadienyl)zirconium dihydride,  
13 (trimethylstannylcyclopentadienyl)(cyclopentadienyl) and  
14 bis(trimethylstannylcyclopentadienyl)zirconium dihydride,  
15 (trimethylplumbylcyclopentadienyl)(cyclopentadienyl) and  
16 bis(trimethylplumbylcyclopentadienyl)zirconium dihydride and the  
17 like; (halogen-substituted-cyclopentadienyl) zirconium compounds such  
18 as (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and  
19 bis(trifluoromethylcyclopentadienyl)zirconium dimethyl  
20 (trifluoromethylcyclopentadienyl)(cyclopentadienyl) and  
21 bis(trifluoromethylcyclopentadienyl)zirconium dihydride and the like;  
22 silyl-substituted bis(cyclopentadienyl) zirconium compounds such as  
23 bis(cyclopentadienyl) (trimethylsilyl)(methyl)zirconium,  
24 bis(cyclopentadienyl) (triphenylsilyl)(methyl)zirconium,  
25 bis(cyclopentadienyl) [tris(dimethylsilyl)silyl](methyl)zirconium,  
26 bis(cyclopentadienyl)[bis(mesityl)silyl](methyl)zirconium,  
27 bis(cyclopentadienyl)(trimethylsilyl)trimethylsilylmethyl zirconium,  
28 bis(cyclopentadienyl) (trimethylsilylbenzyl) and the like;  
29 (bridged-cyclopentadienyl)zirconium compounds such as methylene  
30 bis(cyclopentadienyl)zirconium dimethyl, ethylene  
31 bis(cyclopentadienyl)zirconium dimethyl, dimethylsilyl  
32 bis(cyclopentadienyl)zirconium dimethyl, methylene  
33 bis(cyclopentadienyl)zirconium dihydride, ethylene  
34 bis(cyclopentadienyl)zirconium dihydride and dimethylsilyl  
35 bis(cyclopentadienyl)zirconium dihydride and the like; zirconacycles

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1 such as bis(pentamethylcyclopentadienyl) zirconacyclobutane,  
2 bis(pentamethylcyclopentadienyl) zirconacyclopentane,  
3 bis(cyclopentadienyl)zirconaindane.  
4 1-bis(cyclopentadienyl)zircona-3-dimethylsila-cyclobutane and the  
5 like; olefin, diolefin and aryne ligand substituted  
6 bis(cyclopentadienyl)zirconium compounds such as  
7 bis(cyclopentadienyl) (1,3-butadiene)zirconium, bis(cyclopentadienyl)  
8 (2,3-dimethyl-1,3-butadiene)zirconium,  
9 bis(pentamethylcyclopentadienyl)(benzyne)zirconium and the like;  
10 (hydrocarbyl)(hydride) bis(cyclopentadienyl)zirconium compounds such  
11 as bis(pentamethylcyclopentadienyl)zirconium (phenyl)(hydride),  
12 bis(pentamethylcyclopentadienyl)zirconium (methyl)(hydride) and the  
13 like; and bis(cyclopentadienyl) zirconium compounds in which a  
14 substituent on the cyclopentadienyl radical is bound to the metal  
15 such as (pentamethylcyclopentadienyl)  
16 (tetramethylcyclopentadienylmethylene) zirconium hydride,  
17 (pentamethylcyclopentadienyl)  
18 (tetramethylcyclopentadienylmethylene)zirconium phenyl and the like.  
19 A similar list of illustrative bis(cyclopentadienyl) hafnium  
20 and bis(cyclopentadienyl)titanium compounds could be made, but since  
21 the lists would be nearly identical to that already presented with  
22 respect to bis(cyclopentadienyl)zirconium compounds, such lists are  
23 not deemed essential to a complete disclosure. Other  
24 bis(cyclopentadienyl)hafnium compounds and other  
25 bis(cyclopentadienyl)titanium compounds as well as other  
26 bis(cyclopentadienyl)zirconium compounds which are useful in the  
27 catalyst compositions of this invention will, of course, be apparent  
28 to those skilled in the art.

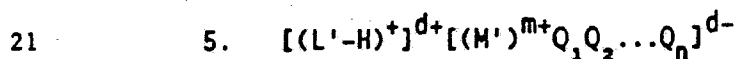
#### The Activator Component

29 Compounds useful as an activator component in the  
30 preparation of the catalyst of this invention will comprise a cation,  
31 which is a Bronsted acid capable of donating a proton, and a  
32 compatible noncoordinating anion containing a single coordination  
33 complex comprising a charge-bearing metal or metalloid core, which

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1 anion is relatively large (bulky), capable of stabilizing the active  
 2 catalyst species (the Group IV-B cation) which is formed when the two  
 3 compounds are combined and said anion will be sufficiently labile to  
 4 be displaced by olefinic, diolefinic and acetylenically unsaturated  
 5 substrates or other neutral Lewis bases such as ethers, nitriles and  
 6 the like. As indicated above, any metal or metalloid capable of  
 7 forming a coordination complex which is stable in water may be used  
 8 or contained in the anion of the second compound. Suitable metals,  
 9 then, include, but are not limited to, aluminum, gold, platinum and  
 10 the like. Suitable metalloids include, but are not limited to,  
 11 boron, phosphorus, silicon and the like. Compounds containing anions  
 12 which comprise coordination complexes containing a single metal or  
 13 metalloid atom are, of course, well known and many, particularly such  
 14 compounds containing a single boron atom in the anion portion, are  
 15 available commercially. In light of this, salts containing anions  
 16 comprising a coordination complex containing a single boron atom are  
 17 preferred.

18 In general, the activator compounds useful in the  
 19 preparation of the catalysts of this invention may be represented by  
 20 the following general formula:



22 Wherein:

23  $L'$  is a neutral Lewis base;  $H$  is a hydrogen atom;

24  $[L'-H]$  is a Bronsted acid;  $M'$  is a metal or metalloid  
 25 selected from the Groups subtended by Groups V-B to V-A of the  
 26 Periodic Table of the Elements; i.e., Groups V-B, VI-B, VII-B,  
 27 VIII-B, I-B, II-B, III-A, IV-A, and V-A;

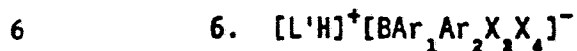
28  $Q_1$  to  $Q_n$  are selected, independently, from the Group  
 29 consisting of hydride radicals, dialkylamido radicals, alkoxide and  
 30 aryloxy radicals, hydrocarbyl and substituted-hydro-carbyl radicals  
 31 and organometalloid radicals and any one, but not more than one, of  
 32  $Q_1$  to  $Q_n$  may be a halide radical - the remaining  $Q_1$  to  $Q_n$   
 33 being, independently, selected from the foregoing radicals;

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1 m is an integer from 1 to 7; n is an integer from 2 to 8;  
2 and  $n - m = d$ .

3

4 The preferred activator compounds comprising boron may be  
5 represented by the following general formula:



7 Wherein:

8  $L'$  is a neutral Lewis base; H is a hydrogen atom;

9  $[L'-H]^+$  is a Bronsted acid; B is boron in a valence state

10 of 3;  $Ar_1$  and  $Ar_2$  are the same or different aromatic or  
11 substituted-aromatic hydrocarbon radicals containing from about 6 to  
12 about 20 carbon atoms and may be linked to each other through a  
13 stable bridging group; and  $X_3$  and  $X_4$  are radicals selected,  
14 independently, from the group consisting of hydride radicals, halide  
15 radicals, with the proviso that only  $X_3$  or  $X_4$  will be halide  
16 at the same time, hydrocarbyl radicals containing from 1 to about 20  
17 carbon atoms, substituted-hydrocarbyl radicals, wherein one or more  
18 of the hydrogen atoms is replaced by a halogen atom, containing from  
19 1 to about 20 carbon atoms, hydrocarbyl-substituted metal  
20 (organometalloid) radicals wherein each hydrocarbyl substitution  
21 contains from 1 to about 20 carbon atoms and said metal is selected  
22 from Group IV-A of the Periodic Table of the Elements and the like.

23 In general,  $Ar_1$  and  $Ar_2$  may, independently, be any  
24 aromatic or substituted-aromatic hydrocarbon radical containing from  
25 about 6 to about 20 carbon atoms. Suitable aromatic radicals  
26 include, but are not limited to, phenyl, naphthyl and anthracenyl  
27 radicals. Suitable substituents include, but are not necessarily  
28 limited to, hydrocarbyl radicals, organometalloid radicals, alkoxy  
29 radicals, alkylamido radicals, fluoro and fluorohydrocarbyl radicals  
30 and the like such as those useful as  $X_3$  and  $X_4$ . The  
31 substituent may be ortho, meta or para, relative to the carbon atoms  
32 bonded to the boron atom. When either or both  $X_3$  and  $X_4$  are

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1 a hydrocarbyl radical, each may be the same or a different aromatic  
2 or substituted-aromatic radical as are  $Ar_1$  and  $Ar_2$ , or the  
3 same may be a straight or branched alkyl, alkenyl or alkynyl radical  
4 having from 1 to about 20 carbon atoms, a cyclic hydrocarbon radical  
5 having from about 5 to about 8 carbon atoms or an alkyl-substituted  
6 cyclic hydrocarbon radical having from about 6 to about 20 carbon  
7 atoms.  $X_3$  and  $X_4$  may also, independently, be alkoxy or  
8 dialkylamido radicals wherein the alkyl portion of said alkoxy and  
9 dialkylamido radicals contain from 1 to about 20 carbon atoms,  
10 hydrocarbyl radicals and organometalloid radicals having from 1 to  
11 about 20 carbon atoms and the like. As indicated above,  $Ar_1$  and  
12  $Ar_2$  may be linked to each other. Similarly, either or both of  
13  $Ar_1$  and  $Ar_2$  could be linked to either  $X_3$  or  $X_4$ .  
14 Finally,  $X_3$  or  $X_4$  may also be linked to each other through a  
15 suitable bridging group.

16 Illustrative, but not limiting, examples of boron compounds  
17 which may be used as an activator component in the preparation of the  
18 improved catalysts of this invention are trialkyl-substituted  
19 ammonium salts such as triethylammonium tetra(phenyl)boron,  
20 tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium  
21 tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron,  
22 trimethylammonium tetra(o-tolyl)boron, tributylammonium  
23 tetra(pentafluorophenyl)boron, tripropylammonium  
24 tetra(o,p-dimethylphenyl)boron, tributylammonium  
25 tetra(m,m-dimethylphenyl)boron, tributylammonium  
26 tetra(p-tri-fluoromethylphenyl)boron, tributylammonium  
27 tetra(pentafluorophenyl)boron, tri(n-butyl)ammonium  
28 tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium salts such as  
29 N,N-dimethylanilinium tetra(phenyl)boron, N,N-diethylanilinium  
30 tetra(phenyl)boron, N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron  
31 and the like; dialkyl ammonium salts such as di(i-propyl)ammonium  
32 tetra(pentafluorophenyl)boron, dicyclohexylammonium  
33 tetra(phenyl)boron and the like; and triaryl phosphonium salts such  
34 as triphenylphosphonium tetra(phenyl)boron,  
35 tri(methylphenyl)phosphonium tetra(phenyl)boron,

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1 tri(dimethylphenyl)phosphonium tetra(phenyl)boron and the like.  
2 Suitable compounds containing other metals and metalloids  
3 which are useful as activator components can be usefully employed.  
4 In this regard, it should be noted that the foregoing list is not  
5 intended to be exhaustive and that other useful boron compounds as  
6 well as useful compounds containing other metals or metalloids would  
7 be readily apparent to those skilled in the art from the foregoing  
8 general equations.

#### The Catalyst Support

9 Typically, the support can be any of the known solid  
10 catalyst supports, particularly porous supports, such as talc,  
11 inorganic oxides, and resinous support materials such as  
12 polyolefins. Preferably, the support material is an inorganic oxide  
13 in particulate form.

14 Suitable inorganic oxide materials which are desirably  
15 employed in accordance with this invention include Group II-A, III-A,  
16 IV-A or IV-B metal oxides. The most preferred catalyst support  
17 materials include silica, alumina, and silica-alumina and mixtures  
18 thereof. Other inorganic oxides that may be employed either alone or  
19 in combination with the silica, alumina or silica-alumina are  
20 magnesia, titania, zirconia, and the like. Other suitable support  
21 materials, however, can be employed, for example, finely divided  
22 polyolefins such as finely divided polyethylene.

23 The metal oxides generally contain surface hydroxyl groups  
24 which may react with and deactivate the ionic metallocene catalyst  
25 when the catalyst is added to the slurried metal oxide support.  
26 Therefore, it is preferred that the inorganic oxide support be  
27 dehydrated prior to use, i.e. subjected to a thermal treatment in  
28 order to remove water and reduce the concentration of the surface  
29 hydroxyl groups. The treatment may be carried out in vacuum or while  
30 purging with a dry inert gas such as nitrogen at a temperature of  
31 about 100°C to about 1000°C, and preferably, from about 300°C to  
32 about 800°C. Pressure considerations are not critical. The duration  
33 of the thermal treatment can be from about 1 to about 24 hours.

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1 However, shorter or longer times can be employed.

2 As an alternative method of dehydration of the metal oxide  
3 support material, chemical dehydration can be advantageously  
4 employed. Chemical dehydration converts all water and hydroxyl  
5 groups on the oxide surface to inert species. Useful chemical agents  
6 are for example, chlorosilanes, such as trimethylchlorosilane, and  
7 the like and alkyl aluminum reagents such as triethyl aluminum and  
8 the like. The chemical dehydration is accomplished by slurring the  
9 inorganic particulate material, such as, for example, silica in an  
10 inert low boiling hydrocarbon, such as, for example, hexane. During  
11 the chemical dehydration reaction, the silica should be maintained in  
12 a moisture and oxygen-free atmosphere. To the silica slurry is then  
13 added a low boiling inert hydrocarbon solution of the chemical  
14 dehydrating agent.

15 The inorganic oxide support used in the preparation of the  
16 catalyst may be any particulate oxide or mixed oxide as previously  
17 described which has been thermally or chemically dehydrated such that  
18 it is substantially free of adsorbed moisture.

19 The specific particle size, surface area and pore volume of  
20 the inorganic oxide determine the amount of inorganic oxide that is  
21 desirable to employ in preparing the catalyst compositions, as well  
22 as affecting the properties of polymers formed with the aid of the  
23 catalyst compositions. These properties must frequently be taken  
24 into consideration in choosing an inorganic oxide for use in a  
25 particular aspect of the invention. In general, optimum results are  
26 usually obtained by the use of inorganic oxides having an average  
27 particle size in the range of about 0.1 to 600 microns, preferably  
28 about 0.3 to 80 microns; a surface area of about 50 to 1,000 square  
29 meters per gram, preferably about 100 to 400 square meters per gram;  
30 and a pore volume of about 0.5 to 3.5 cc per gram; preferably about  
31 0.5 to 2 cc per gram.

#### Catalyst Preparation and Use

32 The supported ionic metallocene catalyst of this invention  
33 may be prepared by combining the metallocene component, the activator

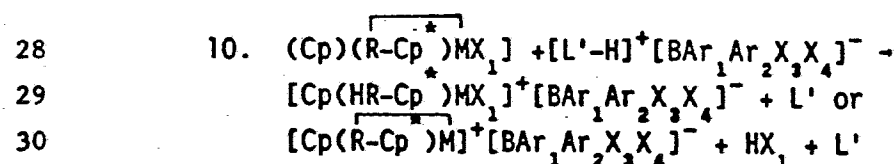
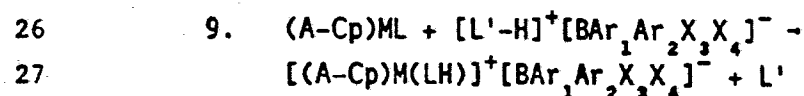
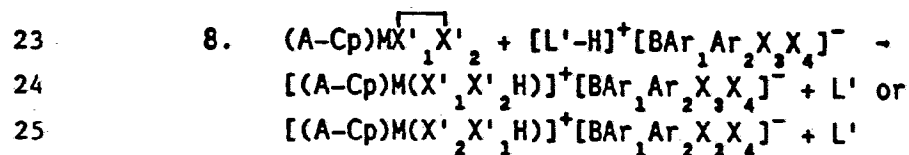
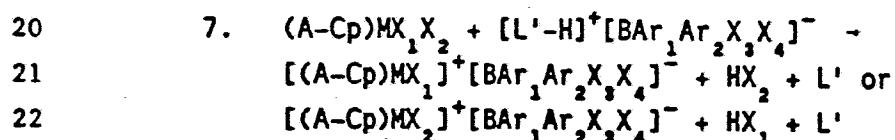
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1 component and the support in suitable solvents in one or more  
2 steps.

### A. Choice of Metallocene-Activator Pairs

3 In general, while most metallocene components identified  
4 above may be combined with most activator components identified above  
5 to produce an active olefin polymerization catalyst, it is desirable  
6 for continuity of the polymerization operations that either the metal  
7 cation initially formed from the metallocene component or a  
8 decomposition product thereof be a relatively stable catalyst. It is  
9 also desirable that the anion of the activator compound be stable to  
10 hydrolysis when an ammonium salt is used. Further, it is desirable  
11 that the acidity of the activator component be sufficient, relative  
12 to the metallocene component to facilitate the needed proton  
13 transfer. In general, bis(cyclopentadienyl) metal compounds which  
14 can be hydrolyzed by aqueous solutions can be considered suitable as  
15 metallocene components to form the catalysts described herein.

16 The chemical reactions which occur in forming the catalyst  
17 of this invention may, when a preferred, boron-containing compound is  
18 used as the second component, be represented by a reference to the  
19 general formulae set forth herein as follows:



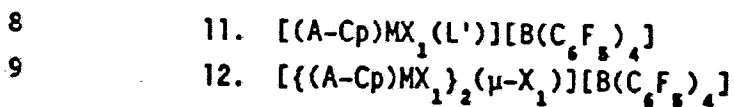
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1           In the foregoing reaction equations the symbols have been  
2 previously defined. In general, the stability and rate of formation  
3 of the products in the foregoing reaction equations, particularly the  
4 metal cation, will vary depending upon the choice of the solvent, the  
5 acidity of the  $[L'-H]^+$  selected, the particular  $L'$ , the anion, the  
6 temperature at which the reaction is completed and the particular  
7 bis(cyclopentadienyl) derivative of the metal selected. Generally,  
8 the initially formed ion-pair will be an active polymerization  
9 catalyst and will polymerize  $\alpha$ -olefins, diolefins, strained cyclic  
10 olefins and acetylenically unsaturated monomers either alone or in  
11 combination with other monomers. In some cases, however, the initial  
12 metal cation will decompose to yield an active polymerization catalyst.

13           With respect to the combination of the metallocene component  
14 with the activator component to form a catalyst of this invention, it  
15 should be noted that the two compounds combined for preparation of the  
16 active catalyst must be selected to avoid transfer of a fragment of  
17 the anion, particularly an aryl group, to the metal cation, thereby  
18 forming a catalytically inactive species. This can be done by steric  
19 hindrance, resulting from substitutions on the cyclopentadienyl carbon  
20 atoms as well as substitutions on the aromatic carbon atoms of the  
21 anion. It follows, then, that the metallocene components comprising  
22 perhydrocarbyl-substituted cyclopentadienyl radicals could be  
23 effectively used with a broader range of activator compounds than  
24 could metallocene components comprising unsubstituted cyclopentadienyl  
25 radicals. As the amount and size of the substitutions on the  
26 cyclopentadienyl radicals are reduced however, more effective  
27 catalysts are obtained with activator compounds containing anions  
28 which are more resistant to degradation, such as those with  
29 substituents on the ortho positions of the phenyl rings. Another  
30 means of rendering the anion more resistant to degradation is afforded  
31 by fluorine substitution, especially perfluoro-substitution, in the  
32 anion. Fluoro-substituted stabilizing anions may, then, be used with  
33 a broader range of metal compound (first components). Activators in  
34 which the anions comprise pentafluorophenyl groups are preferred for  
35 preparing ion-pair metallocene catalysts of this invention.

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1 It is preferred that the mole ratio of metallocene component  
 2 to activator component be 1:1 or greater. In a reaction corresponding  
 3 to general formula 1, when the anion comprises pentafluorophenyl  
 4 groups, two structurally distinct forms of thermally stable ionic  
 5 catalysts have been identified by NMR spectroscopy and are shown in  
 6 general formulae 5 and 6, using tetrakis(pentafluorophenyl)boron as a  
 7 representative anion:



10 In the foregoing formulae, the symbols A-Cp, M, L', and  $X_1$   
 11 correspond to the definitions set forth in general formulae 1-4. The  
 12 symbol "Y" indicates the ligand  $X^1$  bridges the two metal  
 13 centers. In both general formulae 5 and 6, NMR experiments indicate  
 14 that the fluorinated boron anion is completely non-coordinating.  
 15 When the molar ratio of metallocene component to activator component  
 16 is 1:1, L' weakly coordinates to and stabilizes the metallocene cation  
 17 when L' is an aniline derivative, for example N,N-dimethylaniline, to  
 18 give an ionic catalyst of general formula 5. When the molar ratio of  
 19 metallocene component to activator component is greater than 1:1 an X  
 20 group, for examples, a methyl group of an excess  
 21  $(A-Cp)M(CH_3)_2$  molecule when  $(A-Cp)M(CH_3)_2$  is the  
 22 metallocene used, weakly coordinates to and stabilizes the  
 23 metallocene cation to give an ionic catalyst of general formula 6.

#### B. Catalyst Preparation

24 The supported catalyst of this invention can be prepared by  
 25 combining the metallocene, activator components and support in one or  
 26 more suitable solvents or diluent. Suitable solvents and/or diluents  
 27 include, but are not necessarily limited to, straight and  
 28 branched-chain hydrocarbons such as isobutane, butane, pentane,  
 29 hexane, heptane, octane and the like; cyclic and  
 30 alicyclic hydrocarbons such as cyclohexane, cycloheptane,  
 31 methylcyclohexane, methylcycloheptane and the like; and aromatic and

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1 alkyl-substituted aromatic compounds such as benzene, toluene, xylene  
2 and the like.

3 It is preferred that the catalyst components be handled in an  
4 inert, moisture-free, oxygen-free environment such as argon, nitrogen  
5 or helium because of the sensitivity of the catalyst components to  
6 moisture and oxygen.

7 In a preferred method, the metallocene and activator  
8 components are combined in a first step in an aromatic solvent to  
9 produce a solution the reaction product. This reaction may be carried  
10 out in the temperature range -100° to about 300°C, preferably about 0°  
11 to about 100°C. Holding times to allow for the completion of the  
12 reaction may range from about 10 seconds to about 60 minutes depending  
13 upon variables such as reaction temperature and choice of reactants.

14 The solution produced by combining the metallocene and  
15 activator components is then contacted with the support. The method  
16 of contact may vary, but it is preferred that the solution be added to  
17 a rapidly stirred slurry of the catalyst support in a hydrocarbon  
18 solvent, preferably an aliphatic solvent and especially pentane.

19 In another preferred method, in a first step, the activator  
20 component is dissolved in an aromatic solvent with the support to  
21 produce a supported activator component. This reaction is carried out  
22 at a temperature sufficient to produce a homogeneous solution of the  
23 activator component, preferably between about 25°C to about 200°C.  
24 The aromatic solvent is then removed to leave a free-flowing supported  
25 material. The supported material is then contacted with the  
26 metallocene component, preferably in an aliphatic solvent to produce  
27 the supported catalyst.

28 Regardless of the method, the active supported catalyst can  
29 be recovered by evaporation of the solvent to obtain a free-flowing  
30 solid or alternatively, the active supported catalyst can be  
31 maintained in its slurry state for direct use.

32 Contact temperatures may range from about 0° to about 100°C  
33 depending upon the solvents used. Contact times may vary from about  
34 10 seconds to about 60 minutes, longer contact times than 60 minutes  
35 not providing any significant additional benefits.

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1           In the preparation of the supported catalyst, the reagents  
2 should be combined to provide a catalyst concentration (metallocene  
3 and activator) on the support of from about 0.01 wt % to about 20 wt  
4 %, preferably about 1 wt % to about 5 wt % based upon the weight of  
5 the support.

6           In a most preferred embodiment of the present invention,  
7 bis(cyclopentadienyl)zirconium dimethyl or  
8 bis(cyclopentadienyl)hafnium dimethyl will be reacted with  
9 N,N-dimethylanilinium tetra(pentafluorophenyl)boron and then contacted  
10 with an alumina, silica or silica-alumina support to produce the most  
11 preferred catalyst of the present invention. The metallocene and  
12 activator components will be combined at a temperature within the  
13 range -100° to about 300°C, preferably from about 0°C to about 100°C,  
14 and preferably in an aromatic hydrocarbon solvent, most preferably  
15 toluene. A nominal holding time within the range from about 10  
16 seconds to about 60 minutes will be sufficient before the mixture is  
17 contacted with a slurry of the dried support material in an aliphatic  
18 solvent for a contacting period of from about 10 seconds to about 60  
19 minutes.

20           In another preferred method, in a first step,  
21 N,N-dimethylanilinium tetra(pentafluorophenyl)boron is dissolved in an  
22 aromatic solvent maintained at a temperature sufficient to dissolve  
23 the activator component. The support is slurried therein and the  
24 activator and support are reacted for about 1 minute to about 1 hour  
25 to produce a supported activator component. The aromatic solvent is  
26 removed to leave a free-flowing support material containing the  
27 activator component. This supported activator component is then  
28 contacted with bis(cyclopentadienyl)zirconium dimethyl or  
29 bis(cyclopentadienyl)hafnium dimethyl, preferably in an aliphatic  
30 solvent to produce the supported catalyst.

31           With either method, the active supported catalyst can be  
32 recovered by evaporation of the solvent to obtain a free-flowing solid  
33 or, alternately, the active supported catalyst can be maintained in a  
34 slurry state for direct use.

### C. Catalyst Use

35           The supported ionic metallocene catalyst may be used to

1 polymerize  $\alpha$ -olefins and acetylenically unsaturated monomers having  
2 from 2 to about 18 carbon atoms and/or diolefins having from 4 to  
3 about 18 carbon atoms either alone or in combination. The catalyst  
4 may also be used to polymerize  $\alpha$ -olefins, diolefins, strained cyclic  
5 olefins and/or acetylenically unsaturated monomers in combination with  
6 other unsaturated monomers. While the catalyst is active for this  
7 broad range of olefinic monomer feedstock,  $\alpha$ -olefin polymerization  
8 is preferred especially the homopolymerization of ethylene or the  
9 copolymerization of ethylene with olefins having from 3 to 10 carbon  
10 atoms.

11 In a preferred embodiment of the present invention, the  
12 metallocene component will be a bis(cyclopentadienyl)-Group IV-B metal  
13 compound containing two, independently, substituted or unsubstituted  
14 cyclopentadienyl radicals and one or two lower alkyl substituents  
15 and/or one or two hydride substituents and the activator component  
16 will be a tri-substituted ammonium salt of a fluorinated tetraphenyl  
17 boron anion. Each of the tri-substitutions in the ammonium cation  
18 will be the same or a different lower alkyl or aryl radical. By lower  
19 alkyl is meant an alkyl radical containing from 1 to 4 carbon atoms.  
20 N,N-dimethylanilinium tetra(pentafluorophenyl)boron is particularly  
21 preferred. Alumina, silica or silica-alumina will be the preferred  
22 support for producing the supported ionic metallocene catalyst.

23 Certain of the catalysts of this invention, particularly  
24 those based on hafnocenes - using the catalyst produced from the  
25 reaction of bis(cyclopentadienyl)hafnium dimethyl and the  
26 tri-substituted ammonium salt of tetra(pentafluorophenyl)boron as an  
27 example - when used as described herein for the polymerization and  
28 copolymerization of  $\alpha$ -olefins, diolefins, and/or acetylenically  
29 unsaturated monomers, in the absence of a chain transfer agent, can  
30 lead to the production of extremely high molecular weight polymers and  
31 copolymers having relatively narrow molecular weight distributions.  
32 In this regard, it should be noted that homopolymers and copolymers  
33 having molecular weights up to about  $2 \times 10^6$  or higher and  
34 molecular weight distributions within the range of about 1.5 to about  
35 3 or greater can be produced with the catalysts of this invention.

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1 Combinations of two or more ionic metallocene catalyst with the  
2 support can be employed in order to obtain broader MWD such as up to  
3 about 15 or greater. Alternatively, two or more separately supported  
4 catalysts can be used to obtain broad MWD polymers and copolymers.

5 Supported catalysts of this invention containing a  
6 metallocene component which is either a pure enantiomer or the racemic  
7 mixture of two enantiomers of a rigid, chiral metallocene can  
8 polymerize prochiral olefins (propylene and higher  $\alpha$ -olefins) to  
9 crystalline polymers including syndiotactic and isotactic polymers.  
10 Bis(cyclopentadienyl)metal compounds in which each of the  
11 cyclopentadienyl radicals is substituted and containing a covalent  
12 bridging group between the two cyclopentadienyl radicals are  
13 particularly useful for isotactic polymerizations of this type.  
14 Prochiral metallocenes, for example those based on complexes of  
15 propyl-2-cyclopentadienyl-2-(1-fluorenyl) hafnium, can be used to  
16 polymerize propylene or higher  $\alpha$ -olefins to syndiotactic polymers.

17 The supported catalysts may be most usefully employed in gas  
18 or slurry phase processes, both of which are known to those of skill  
19 in the art. Thus, polymerizations using the invention supported  
20 catalysts may be conducted by either of these processes, generally at  
21 a temperature in the range of about 0°-160°C or even higher, and under  
22 atmospheric, subatmospheric, or superatmospheric pressure conditions.

23 A slurry polymerization process can utilize sub- or  
24 super-atmospheric pressures and temperatures in the range of  
25 -80-250°C. In a slurry polymerization, a suspension of solid,  
26 particulate polymer is formed in a liquid polymerization medium to  
27 which ethylene,  $\alpha$ -olefin, diolefin, cyclic olefin or acetylenically  
28 unsaturated comonomer, hydrogen and catalyst are added. Alkanes and  
29 cycloalkanes, such as butane, pentane, hexane, or cyclohexane, are  
30 preferred with C<sub>4</sub> to C<sub>10</sub> alkanes especially preferred.  
31 Preferred solvents also include liquid olefins which may act as  
32 monomers or comonomers including ethylene, propylene, butadiene,  
33 cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene,  
34 1,4-hexadiene, 1-octene, 1-decene and the like.

35 A gas-phase polymerization process utilizes superatmospheric

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1 pressure and temperatures in the range of about 50° - 120°C.  
2 Gas-phase polymerization can be performed in a stirred or fluidized  
3 bed of catalyst and product particles in a pressure vessel adapted to  
4 permit the separation of product particles from unreacted gases.  
5 Thermostated ethylene, comonomer, hydrogen and an inert diluent gas  
6 such as nitrogen can be introduced or recirculated so as to maintain  
7 the particles at a temperature of 50° - 120°C. Polymer product can be  
8 withdrawn continuously or semi-continuously at a rate such as to  
9 maintain a constant product inventory in the reactor. After  
10 polymerization and deactivation of the catalyst, the product polymer  
11 can be recovered by any suitable means. In commercial practice, the  
12 polymer product can be recovered directly from the gas phase reactor,  
13 freed of residual monomer with a nitrogen purge, and used without  
14 further deactivation or catalyst removal. The polymer obtained can be  
15 extruded into water and cut into pellets or other suitable comminuted  
16 shapes. Pigments, antioxidants and other additives, as is known in  
17 the art, may be added to the polymer.

18 While it is a characteristic of the invention supported  
19 catalyst that the produced polymers have a narrow molecular weight  
20 distribution, broad molecular weight distribution polymers may be  
21 produced by using two or more metallocenes or two or more activators.

22 The advantages of the instant invention will be more readily  
23 appreciated by reference to the following illustrative, non-limiting  
24 examples.

#### Example 1

25 A supported catalyst was prepared by reacting  
26 bis(cyclopentadienyl)hafnium dimethyl (30 mg) with  
27 N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (60 mg) in  
28 toluene (8 ml). This solution was added slowly to a suspension of  
29 basic alumina (Brockman Activity I, dried overnight at 100°C under  
30 vacuum; 2.0 g) in pentane (25 ml). The mixture was allowed to stir  
31 for about 3 minutes at room temperature. The supernatant solution was  
32 then decanted from the solid material and the solids reslurried with  
33 fresh pentane. The supernatant solution was again decanted from the

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1 solids and the solids suspended in fresh pentane (ca. 30 ml). This  
2 suspension was transferred, under nitrogen, by means of a double-ended  
3 needle into a 1 liter stainless-steel autoclave containing 400 ml of  
4 dry, deoxygenated hexane and which had been previously flushed with  
5 nitrogen. The autoclave was then pressured to 90 psig with ethylene  
6 and stirred at 40°C. After 30 minutes, the autoclave was cooled,  
7 vented and the contents separated by filtration. The yield of linear  
8 granular, free-flowing polyethylene was 11.2 g. The polymer had a  
9 weight-average molecular weight of 594,000 and a molecular weight  
10 distribution of 2.15.

#### Example 2

11 The supported catalyst of Example 1 was used to polymerize  
12 ethylene in a process similar to that of Example 1 except that the  
13 autoclave was pressured to 300 psig of ethylene. The yield of linear  
14 granular, free-flowing polyethylene was 48.5 g with a bulk density of  
15 0.17 g/cc versus 0.07 g/cc when an unsupported, homogeneous catalyst  
16 is used.

#### Example 3

17 A supported catalyst was prepared by reacting  
18 bis(cyclopentadienyl)zirconium dimethyl (20 mg) with  
19 N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (60 mg) in  
20 toluene (20 ml). This solution was added slowly to a suspension of  
21 basic alumina (2.0 g) in pentane (25 ml). The mixture was allowed to  
22 stir for about 3 minutes at room temperature. The supernatant  
23 solution was decanted from the solid material and the solids  
24 reslurried with fresh pentane. The supernatant solution was again  
25 decanted from the solids and the solids were suspended in fresh  
26 pentane (ca. 30 ml). This suspension was transferred, under nitrogen,  
27 by means of a double-ended needle into a 1 liter stainless-steel  
28 autoclave, previously flushed with nitrogen, containing 400 ml of dry,  
29 deoxygenated hexane. The autoclave was then pressured to 400 psig  
30 with ethylene and stirred at 40°C. After 30 minutes, the autoclave  
31 was cooled and vented and the contents isolated by filtration. The

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1 yield of linear granular, free-flowing polyethylene was 4.7 g with a  
2 weight-average molecular weight of 515,000 and a MWD of 1.74.

#### Example 4

4 A supported catalyst was prepared as in Example 1 except that  
5 2.0 g of Davison 948 silica (dried at 800°C with a nitrogen purge) was  
6 used in place of alumina. The catalyst was used to polymerize  
7 ethylene in a process similar to that of Example 2. The yield of  
8 linear granular, free-flowing polyethylene was 11.1 g with a  
9 weight-average molecular weight of 1,384,000 and a MWD of 1.67.

#### Example 5

10 A supported catalyst was prepared as in Example 4 except that  
11 20 mg of bis(cyclopentadienyl)zirconium dimethyl was used in place of  
12 bis(cyclopentadienyl)hafnium dimethyl. This catalyst was used to  
13 polymerize ethylene in a process similar to that of Example 2. The  
14 yield of linear granular, free-flowing polyethylene formed was 2.7 g  
15 with a weight-average molecular weight of 759,000 and a MWD of 1.67.

#### Example 6

16 A supported catalyst was prepared by reacting  
17 bis(cyclopentadienyl)hafnium dimethyl (45 mg) with  
18 N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (90 mg) in  
19 toluene (20 ml). This solution was added slowly to a suspension of  
20 basic alumina (3.0 g) in pentane (25 ml). The mixture was allowed to  
21 stir for about 3 minutes at room temperature. The solution was  
22 decanted from the solid material and the solids reslurried with fresh  
23 pentane. The supernatant solution was again decanted from the solids  
24 and the solids were dried in an atmosphere of nitrogen. This  
25 suspension was injected into a 1 liter stainless-steel autoclave,  
26 previously flushed with nitrogen, containing 300 ml of propylene, by  
27 washing 50 ml of propylene through a stainless-steel catalyst addition  
28 tube containing the solid catalyst. The autoclave was then pressured  
29 to 100 psig with ethylene and stirred at 50°C. After 15 minutes, the  
30 autoclave was cooled and vented and the polymer product was isolated.

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1 The yield of granular ethylene-propylene copolymer was 38 g. This  
2 polymer, which contained 21 wt. % ethylene, had a weight-average  
3 molecular weight of 423,000 and a molecular weight distribution of  
4 2.88.

#### Example 7

5 Ethylene and propylene was copolymerized in a manner similar  
6 to Example 6, with the exceptions that the ethylene pressure was  
7 increased to 200 psig and the autoclave was heated to 45°C. The yield  
8 of granular ethylene-propylene copolymer was 57.1 g. This polymer,  
9 which contained 52 wt. % ethylene, had a weight-average molecular  
10 weight of 1,006,000 and a molecular weight distribution of 2.01.

#### Example 8

11 A supported catalyst of this invention was prepared by  
12 reacting rac-dimethylsilylbis(indenyl)hafnium dimethyl (29 mg) with  
13 N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (45 mg) in  
14 toluene (10 ml). This solution was added slowly to a suspension of  
15 basic alumina (1.5 g) in pentane (25 ml). The mixture was allowed to  
16 stir for about 3 minutes at room temperature. The supernatant  
17 solution was decanted from the solid material and the solids  
18 reslurried with fresh pentane. The supernatant solution was again  
19 decanted from the solids and the solids were suspended in fresh  
20 pentane (ca. 30 ml). This suspension was transferred under nitrogen,  
21 by means of double-ended needle into a 1 liter stainless-steel  
22 autoclave, previously flushed with nitrogen, containing 400 ml of dry,  
23 deoxygenated hexane. Propylene (200 ml) was added to the autoclave,  
24 which was stirred at 50°C. After 1.75 hours, the autoclave was cooled  
25 and vented and the contents separated by filtration. The yield of  
26 isotactic polypropylene was 9.5 g. This polymer had a melting point  
27 of 127°C, as determined by differential scanning calorimetry, a weight  
28 average molecular weight of 181,000 and a molecular weight  
29 distribution of 1.95. Analysis by C-13 NMR spectroscopy indicated  
30 that the polypropylene was 92% isotactic.

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Example 9

1           A 1 liter stainless-steel autoclave was charged with virgin  
2 polypropylene (14 mesh, 190 g) and heated to 85°C under a dynamic  
3 nitrogen purge. After cooling to 50°C, the catalyst of Example 1 (2.0  
4 g) was added to the reactor from a stainless-steel catalyst addition  
5 tube using high-pressure nitrogen. After venting off the excess  
6 nitrogen pressure, ethylene was admitted to the stirred polymer bed to  
7 maintain a constant flow. The pressure inside the autoclave ranged  
8 from 10 to 35 psig. The maximum temperature in the autoclave reached  
9 70°C. After 1 hour, the autoclave was cooled and vented and the  
10 polymer mixture isolated. The net increase in the polymer weight was  
11 38 g. A portion of the polyethylene was sieved from the polypropylene  
12 stirring aid and was found to have a weight-average molecular weight  
13 of 175,000 and a MWD of 2.53.

Example 10

14           Alumina (1.0 g), slurried in 10 ml of pentane, was treated  
15 for 15 minutes with 1 ml of a 1 M solution of triethylaluminum in  
16 hexane. The support was separated from the liquid by decantation,  
17 washed twice with 10 ml of pentane and dried in vacuo.

18           N,N-dimethylanilinium tetrakis (pentafluorophenyl)boron (30  
19 mg) was heated in toluene (25 ml) to produce a homogeneous solution.  
20 The warm solution was added dropwise to the support prepared as  
21 described above. The solvent was removed in vacuo to leave a  
22 free-flowing supported material.

23           This support material (1.0 g) was slurried in 10 ml of  
24 pentane. To this was added dropwise 5 ml of a pentane solution  
25 containing bis(cyclopentadienyl) hafnium dimethyl (15 mg). After  
26 stirring at room temperature for 15 minutes, the solvent was removed  
27 in vacuo to leave a free-flowing supported catalyst.

Example 11

28           500 mg. of the supported catalyst of Example 10 was used to  
29 polymerize ethylene in a process similar to Example 1 except that the  
30 autoclave was pressured to 400 psig with ethylene and was heated to

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1 80°C. The yield of linear granular, free-flowing polyethylene was 132  
2 g.

3 Although the invention has been described with reference to  
4 its preferred embodiments, those of ordinary skill in the art may,  
5 upon reading this disclosure, appreciate changes and modifications  
6 which do not depart from the scope and spirit of the invention as  
7 described above or claimed hereafter.

#### Example 12

8 Davison 952 silica (1 g) was slurried in pentane  
9 and treated with 1 ml of a 1 m solution of triethylaluminum  
10 in hexane. The support was separated from the liquid by  
11 decantation, washed twice with pentane and dried in vacuo.

12 N,N-dimethylanilinium tetrakis  
13 (pentafluorophenyl)boron (30 mg) was heated in toluene to  
14 produce a homogeneous solution. The warm solution was added  
15 dropwise to the support prepared as described above. The  
16 solvent was removed in vacuo to leave a free-flowing  
17 supported material.

18 This support material was slurried in 10 ml of  
19 pentane. To this was added dropwise 10 ml of a pentane  
20 solution containing 15 mg of rac-  
21 dimethylsilylbis(tetrahydroindenyl) - zirconium dimethyl.  
22 After stirring at room temperature for 15 minutes, the  
23 solvent was removed in vacuo to leave a free-flowing  
24 supported catalyst.

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Example 13

1           The catalyst of Example 12 (887 mg) was injected  
2 by means of high-pressure nitrogen into a 1 liter stainless-  
3 steel autoclave, which was previously flushed with nitrogen,  
4 containing 300 ml dry, deoxygenated propylene at 40 degrees  
5 C. After 20 minutes, the contents isolated the yield of  
6 isotactic polypropylene was 101.7 g.

Example 14

7           Davison 948 silica (3 g), dehydrated at 800  
8 degrees with an nitrogen purge was slurried in pentane and  
9 treated with 8 ml of a 1.5 M solution of triethylaluminum in  
10 hexane. The support was separated from the liquid by  
11 decantation, washed six times with pentane, and dried in  
12 vacuo.

13           N,N-dimethylanilinium  
14 tetrakis(pentafluorophenyl)baron (96 mg) was heated in 30 ml  
15 warm toluene, to produce a homogeneous solution. The warm  
16 solution was added dropwise to a toluene slurry of the  
17 support prepared as described above. The solvent was  
18 removed in vacuo with gentle heating to leave a free-flowing  
19 supported material.

20           This supported material was reslurried in pentane.  
21 To this was added dropwise 20 ml of a pentane solution  
22 containing 48 mg of bis(cyclopentadienyl)hafnium dimethyl.  
23 After stirring at room temperature for 15 minutes, the  
24 solvent was removed in vacuo to leave a free-flowing  
25 supported catalyst.

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Example 15

1           The catalyst of Example 14 (100 mg) was injected  
2 with 100 ml hexane into a 1 liter stainless-steel autoclave,  
3 which was previously flushed with nitrogen, containing 300  
4 ml of dry, deoxygenated hexane and pressurized with 200 psi  
5 ethylene at 60 degrees C. After 20 minutes the autoclave  
6 was cooled and vented and the contents isolated by  
7 filtration. The yield of linear polyethylene was 78.7 g.

CLAIMS:

1. A method for preparing a supported ionic catalyst comprising the steps of:

(a) combining, in a solvent or diluent

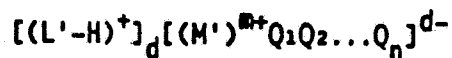
(i) at least one metallocene component comprising a bis(cyclopentadienyl)metal compound containing at least one ligand capable of reacting with a proton, said metal being selected from the group consisting of titanium, zirconium and hafnium,

(ii) at least one activator component comprising a cation capable of donating a proton and an anion, said anion being a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, said anion being bulky, labile and capable of stabilizing the metal cation formed as a result of reaction between the two, and

(iii) a catalyst support material suspended in a suitable solvent; and

(b) recovering a supported catalyst product as a free-flowing solid or slurry.

2. The method of claim 1 wherein said activator component is represented by the following general formula:



wherein:

L' is a neutral Lewis base; H is a hydrogen atom;

[L'-H]<sup>+</sup> is a Bronsted acid;

M' is a metal or metalloid selected from the groups subtended by Groups V-B to V-A of the Periodic Table of the Elements; i.e., Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A and V-A;

Q<sub>1</sub> to Q<sub>n</sub> are selected, independently, from the group consisting of hydride radicals, dialkylamido radicals, alkoxide and

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aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals and organometalloid radicals and any one, but not more than one, of  $Q_1$  to  $Q_n$  may be a halide radical with the remaining  $Q_1$  to  $Q_n$  being, independently, selected from the foregoing radicals;

$m$  is an integer from 1 to 7;  $n$  is an integer from 2 to 8; and  $n - m = d$ .

3. The method of claim 2 wherein said activator component is represented by the following general formula:

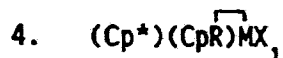
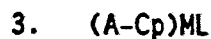
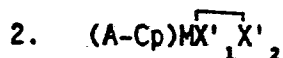
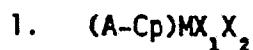


wherein:

$L'$  is a neutral Lewis base;  $H$  is a hydrogen atom;  
 $[L'-H]^+$  is a Bronsted acid;  $B$  is boron in a valence state of 3;

$Ar_1$  and  $Ar_2$  are the same or different aromatic or substituted-aromatic hydrocarbon radicals, said radicals being optionally linked to each other through a stable bridging group; and  $X_3$  and  $X_4$  are, independently, selected from the group consisting of hydride radicals, halide radicals, hydrocarbyl and substituted-hydrocarbyl radicals and organometalloid radicals.

4. The method of claim 3 wherein said bis(cyclopentadienyl)metal compound is represented by one of the following general formulae:



Wherein:

M is a metal selected from the group consisting of titanium, zirconium and hafnium;

(A-Cp) comprises (Cp)(Cp\*) or Cp-A'-Cp\* and Cp and Cp\* are the same or different substituted or unsubstituted cyclopentadienyl radicals;

A' is a covalent bridging group; L is an olefin, diolefin or aryne ligand;

X<sub>1</sub> and X<sub>2</sub> are, independently, selected from the group consisting of hydride radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals and organometalloid radicals;

X'<sub>1</sub> and X'<sub>2</sub> are joined and bound to the metal atom to form a metallacycle, in which the metal atom, X'<sub>1</sub> and X'<sub>2</sub> form a hydrocarbocyclic ring containing from about 3 to about 20 carbon atoms; and

R is a substituent on one of the cyclopentadienyl radicals which is also bound to the metal atom.

5. The method of claim 1 wherein said support is selected from alumina, silica, alumina-silica, talc, magnesia, zirconia, titania, finely divided polyolefins or mixtures thereof.

6. The method of claim 5 wherein said support is alumina, silica or mixtures thereof.

7. The method of claim 4 wherein the metallocene is bis(cyclopentadienyl)zirconium dimethyl or bis(cyclopentadienyl)hafnium dimethyl; the activator is N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron; and the support is alumina or silica.

8. The method in of claim 1, wherein the at least one metallocene and the at least one activator component are reacted in a solvent or diluent and the direct product or the decomposition product of said direct product is contacted in a suitable solvent with a

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catalyst support material and thereafter the supported catalyst product is recovered as a free-flowing solid or slurry.

9. The method of claim 1, wherein the activator component is dissolved in an aromatic solvent and the support is slurried therein and allowed to react, the supported activator component is then contacted with the metallocene component in an aliphatic method.

10. A catalyst comprising the supported ionic catalyst obtained by the method of claim 1.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/07669

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to international Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>5</sup> : C 08 F 4/76, 4/603, 10/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>5</sup>	C 08 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>9</sup>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	EP, A, 0277004 (EXXON) 3 August 1988 see the claims cited in the application --	1
A	EP, A, 0232595 (EXXON) 19 August 1987 see the claims cited in the application --	1
A	EP, A, 0277003 (EXXON) 3 August 1988 see the claims --	1
A	US, A, 4017525 (R.A. SETTERQUIST) 12 April 1977 see the claims -----	1
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
18th April 1991		13. 06. 91
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		miss T. MORTENSEN 

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9007669  
SA 44096

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/06/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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EP-A- 0232595	19-08-87	US-A- 4701432 AU-B- 599622 AU-A- 6728587 EP-A- 0245482 JP-T- 63501369 WO-A- 8702991	20-10-87 26-07-90 02-06-87 19-11-87 26-05-88 21-05-87
EP-A- 0277003	03-08-88	AU-A- 1294588 JP-T- 1501950 WO-A- 8805792	24-08-88 06-07-89 11-08-88
US-A- 4017525	12-04-77	None	